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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

A number of polymers derived from 2,5-dialkoxy-1,4-bis(2-thienyl)benzene have been prepared and studied. Symmetric polymer repeat units are obtained when the alkoxy substituents are equivalent and asymmetric repeat units when they are different. The symmetric polymers are partially crystalline whereas the asymmetric ones are completely amorphous. Interestingly, the former show a higher conductivity than the latter upon doping. A new type of chemical sensor has been developed based on the redox release of fluorophores from a conducting polymer. Sub ppm levels of several analytes have been measured. 5-Decylbenzo[c]-2',5'-dihydrothiophene has been prepared and polymerized to processable poly(5-decylbenzo[c]thiophene). This is a low band-gap polymer whose color gets much lighter upon doping. Another low band-gap polymer, poly(2,3-dihexylthieno[3,4-b]pyrazine) has been prepared and is also being investigated.

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Technical Report No. 23

Electronic and Ionic Transport in Processable Conducting Polymers

by

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October 5, 1990

Description of Progress

The effect of symmetric repeat units along a conjugated polymer has been studied in a series of bis(2-thienyl)benzene polymers that are 2,5-dialkoxy substituted on the benzene ring. The long chain (C_7 and C_{12}) alkoxy substituents impart solution processability to the polymer and, when symmetrically substituted, isoregic polymers that are partially crystalline are obtained. When the monomers are asymmetrically substituted, aregic and amorphous polymers are obtained. In addition to having an impact on thermal properties, regiospecificity has an effect on electrical properties. After solution doping with $NO^+PF_6^-$ the symmetrically substituted polymers exhibit a conductivity approximately 1 order of magnitude higher than the asymmetrically substituted analogues.

A new type of chemical sensor has been developed based on the redox release (by the analyte) of fluorophores from a conducting polymer thin film. Proof-of-concept measurements have been completed for polypyrrole/naphthalene sulfonate (NS^-) thin films and hydrazine and sulfite as analytes. Fluorometric detection of the chemically released NS^- species affords an extremely sensitive (sub ppm) probe of the hydrazine or sulfite concentration in the solution contacting the polymer thin film.

Ion transport measurements on polypyrrole/naphthalene sulfonate thin films continue as do the immobilization of macrocyclic complexes at chemically-modified polymer surfaces. The transport measurements will be extended to flow geometries using equipment being currently assembled.

A synthesis of 5-decylbenzo[c]-2',5'-dihydrothiophene has been carried out and this monomer has been polymerized to soluble poly(5-decylbenzo[c]thiophene) [poly(5-decyliso-thianaphthene)] with $FeCl_3/O_2$. Very preliminary studies have provided a weight average molecular weight (vs. polystyrene) of 25,000 with initial multiangle laser light scattering giving a value >100,000 and the spectra are consistent with the structure. A chloroform solution of the polymer is dark blue-black (λ_{max} = 512 nm) and as a film the absorption edge (band-gap) is about 1.0-1.3 eV consistent with the theoretical calculations which we have published. When doped

with $NO^+BF_4^-$ the solution becomes much lighter and yellow in color with a new absorption at 1200 nm.

A synthesis of 2,3-dihexylthieno[3,4-b]pyrazine has also been carried out and this monomer has also been polymerized using $FeCl_3/O_2$ or electrochemically, to soluble poly(2,3-dihexylthieno[3,4-b]pyrazine). Very preliminary studies have shown that the spectra agree with the structure, the UV-VIS maximum ($CHCl_3$ solution) is at 800 nm with the absorption edge at ca. 1.2 eV. This is, as expected for the solution, somewhat higher than our published calculated value for the band-gap. Doping with $NO^+BF_4^-$ resulted in a lighter colored solution with λ_{max} at 1600 nm. Further studies on these two low band-gap polymers are in progress.

Publications

Papers Published

Gieselman, M. G. and Reynolds, J. R. "Poly(*p*-phenyleneterephthalamide propane sulfonate): A New Polyelectrolyte for Application to Conducting Molecular Composites," *Macromolecules* **1990**, *23*, 3118-3124.

Wang, F. and Reynolds, J. R. "Soluble and Electroactive Nickel Bis(dithiolene) Polymers Prepared Via Metal Complexation Polymerization," *Macromolecules* **1990**, *23*, 3219-3225.

Basak, S.; Rajeshwar, K. and Kaneko, M. "Ion Binding by Poly{pyrrole-co-[3-(pyrrol-1-yl)propanesulfonate]} Thin Films," *Anal. Chem.* **1990**, *62*, 1407-1413.

Papers in Press

Reynolds, J. R. and Pomerantz, M. "Processable Electronically Conducting Polymers," in *Electroresponsive Molecular and Polymeric Systems*; Skotheim, T. A., Ed.; Marcel Dekker: New York; Vol. 2, in press.

Jolly, C. A. and Reynolds, J. R. "Mechanically Durable, Semiconducting and Optically Polarizing Poly(nickel tetrathiooxalate)/Poly(vinyl alcohol) Composites," *Chem. of Materials*, in press.

Reynolds, J. R.; Ruiz, J. P.; Child, A. D.; Marynick, D. S. and Nayak, K. "Electrically Conducting Polymers Containing Alternating Substituted Phenylenes and Bithiophene Repeat Units," *Macromolecules*, in press.

Sundaresan, N. S.; Reynolds, J. R. and Ruiz, J. P. "Photocurrent Response of Poly(3-ethylmercaptothiophene," *J. Mat. Sci.*, in press.

Basak, S.; Rajeshwar, K. and Kaneko, M. "In Situ Photogeneration of a Catalyst on a Chemically-Modified Electrode Surface: Application to a Mixed Valent Hexacyanoferrate System," *J. Electroanal. Chem.*, in press.

Papers Submitted for Publication

Baker, C. K. and Reynolds, J. R. "Electrochemically Induced Mass Transport in Poly(pyrrole)/ Poly(styrene sulfonate) Molecular Composites," *J. Phys. Chem.*, submitted for publication.

Qiu, Y. J. and Reynolds, J. R. "Dopant Anion Controlled Ion Transport Behavior of Polypyrrole," *Polym. Eng. and Sci.*, submitted for publication.

Stickle, W. F.; Reynolds, J. R. and Jolly, C. A. "Surface Characterization of Electrically Conducting Nickel Tetrathiooxalate/Poly(Vinyl Alcohol) Composites," *Langmuir*, submitted for publication.

Wang, F.; Qiu, Y. J. and Reynolds, J. R. "Synthesis and Characterization of Nickel Bis(dithiolene) Complex Polycarbonates and Polyurethanes," *Macromolecules*, submitted for publication.

Qiu, Y. J. and Reynolds, J. R. "Charge and Ion Transport in Poly(pyrrole copper phthalocyaninesulfonate) During Redox Switching," *J. Electroanal. Chem.*, submitted for publication.

Pomerantz, M.; Tseng, J. J.; Zhu, H.; Sproull, S. J.; Reynolds, J. R.; Uitz, R.; Arnott, H. J. and Haider, M. I. "Processable Polymers and Copolymers of 3-Alkylthiophenes and Their Blends," *Synth. Met.*, submitted for publication.

Krishna, V.; Ho, Y.-H.; Basak, S. and Rajeshwar, K. "A Luminescence Probe and Voltammetry Study of Ion Transport During Redox Switching of Polypyrrole Thin Films," *J. Am. Chem. Soc.*, submitted for publication.

Reynolds, J. R.; Ruiz, J. P.; Nayak, K.; Child, A. D. and Marynick, D. S. "Electrically Conducting Polymers Containing Alternating Substituted Phenylene and Heterocycle Repeat Units," *Synth. Met.*, submitted for publication.

Prczyna, L. A.; Wnek, G. E.; Lee, J. J.; Reynolds, J. R. and Qiu, Y. J. "Interaction of Cationic Proteins with Electroactive Polypyrrole/Poly(styrene sulfonate) and Poly(*N*-methylpyrrole/Poly (styrene sulfonate) Films," *Synth. Met.* submitted for publication.

Meetings Attended and Papers and Talks Presented

John Reynolds, a postdoctoral associate, John Tseng, and three graduate students, Melinda Gieselman, Y. J. Qiu and Fei Wang, attended the 33rd International Union of Pure and Applied Chemistry (IUPAC) Symposium on Macromolecules (MACRO 90) in Montréal, Québec, Canada, on July 9-13, 1990. The following papers were presented:

Pomerantz, M.; Tseng, J. J.; Zhu, H. and Sproull, S. J. "Molecular Weight Studies of Soluble 3-Alkylthiophene Polymers and Copolymers."

Reynolds, J. R.; Ruiz, J. P.; Nayak, K.; Child, A. D. and Marynick, D. S. "Electrically Conducting Polymers Containing Alternating Substituted Phenylene and Heterocycle Repeat Units."

Reynolds, J. R. and Gieselman, M. B. "New Polyelectrolytes for Application to Polypyrrole Composites."

Reynolds, J. R. and Qiu, Y. J. "Dopant Ion Controlled Ion Transport Behavior of Polypyrrole."

Reynolds, J. R. and Wang, F. "Soluble and Electroactive Nickel Bis(dithiolene) Polymers."

Martin Pomerantz and John Reynolds attended the International Conference on Science and Technology of Synthetic Metals (ICSM '90) in Tübingen, West Germany, on September 3-7, 1990. The following invited papers were presented:

Pomerantz, M.; Tseng, J. J.; Zhu, H. and Sproull, S. J. "Molecular Weight Studies of Soluble 3-Alkylthiophene Polymers and Copolymers."

Reynolds, J. R.; Ruiz, J. P.; Nayak, K.; Child, A. D. and Marynick, D. S. "Electrically Conducting Polymers Containing Alternating Substituted Phenylene and Heterocycle Repeat Units."

In addition, the following paper on collaborative work with Gary Wnek, Rennselaer Polytechnic Institute, was presented:

Prezyna, L. A.; Wnek, G. E.; Lee, J. J.; Reynolds, J. R. and Qiu, Y. J. "Interaction of Cationic Proteins with Electroactive Polypyrrole/Poly(styrene sulfonate) and Poly(*N*-methylpyrrole)/Poly (styrene sulfonate) Films."

John Reynolds and Martin Pomerantz are writing a report detailing the research presentations at this meeting (ICSM '90) for the *ESN Information Bulletin*, published by the ONR European Office in London.

Krishnan Rajeshwar attended the 177th National Meeting of the Electrochemical Society, Montréal, Québec, Canada, May, 1990, where he presented the following paper:

Basak, S.; Rajeshwar, K. and Kaneko, M. "Ion Binding by Poly{pyrrole-co-[3-(pyrrol-1-yl)propanesulfonate]} Thin Films."

John Reynolds visited Wright Patterson Air Force Base, Dayton, Ohio, on June 12, 1990, and presented a seminar on DARPA funded conducting polymer research.

John Reynolds and Dennis Marynick visited the U. S. Army Ballistics Research Laboratory, Aberdeen Proving Grounds, Maryland, on June 20, 1990. John Reynolds presented a seminar on conducting and dielectric polymer research funded by DARPA.

John Reynolds presented a seminar on DARPA funded conducting polymer work at the Naval Air Development Center, Warminster, Pennsylvania, on August 16, 1990. Discussions between The University of Texas at Arlington, General Dynamics and NADC researchers were directed to future joint programs.

Martin Pomerantz presented a seminar describing our DARPA funded conducting polyheterocycle research at The Hebrew University of Jerusalem, Jerusalem, Israel, July 30, 1990.

Krishnan Rajeshwar presented an invited talk at the Texas Chemistry Forum held at The University of Texas at Austin, May 1990, entitled "Charge Transport/Storage in Biconductive Oxides and Polymers."

Visitors to The University of Texas at Arlington

Dr. Francis Garnier, CNRS, Thiais, France, visited The University of Texas at Arlington on July 24, 1990, and gave a seminar detailing his research on substituted polythiophenes.

Professor P. S. Zacharias, who is currently a visiting professor from Central University, Hyderabad, India, presented a seminar entitled "Electrochemistry of Copper Macrocyclic Complexes" on September 21, 1990.

Personnel Changes

Professor P. S. Zacharias has joined our group as a Visiting Professor from Central University, Hyderabad, India.

Dr. Sung Hong, Ph. D. from Case Western Reserve University, has joined our group as a Postdoctoral Associate.

Dr. John J. Tseng, postdoctoral associate, left for a position at Atochem North America, Inc.